Electrochemical Polymerization of Pyrrole on Polymer-coated Electrodes

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The electrochemical polymerization of pyrrole on an electrode coated with an insulating polymer film produces electrically conducting polymer alloys of the insulating polymer and polypyrrole.

Numerous studies have been carried out in an attempt to add high electrical conductivity to organic polymers.[1,2] In this communication we describe a new approach for realizing highly electrically conducting polymers. Our method is the electrochemical doping of electrically conducting polypyrrole into polymer films coated on an electrode surface. In principle, almost all polymer films will be easily converted into highly conducting films by this method.

It is well known that pyrroles or thiophenes are electrochemically polymerized on electrode surfaces, forming electrically conducting films.[3] These polymers are deeply coloured owing to simultaneous anion doping, and they are relatively

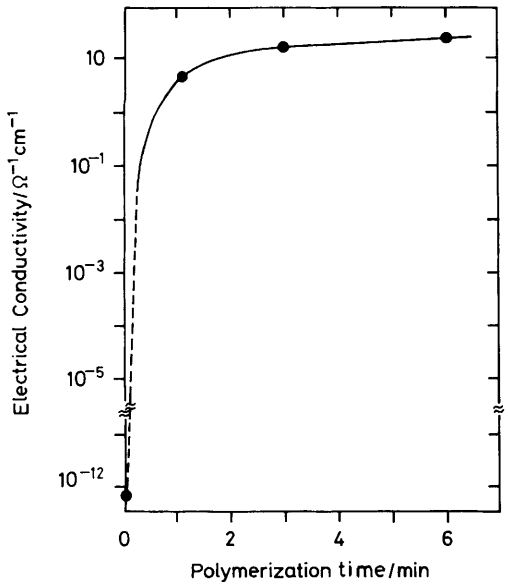

Figure 1. Electrical conductivity of the poly(vinyl chloride) film as a function of the time of the electrochemical polymerization of pyrrole.

stable. We attempted the electrochemical polymerization of pyrrole on an electrode substrate the surface of which was coated with an electrochemically-inactive insulating polymer film. When the electrolytic solution is suitably prepared according to the kind of polymer used, the polymerization of pyrrole occurs even on the insulated substrate. The resultant polymer film is a mixture of polypyrrole and the base polymer, and shows a high electrical conductivity. The electrolytic solution, an acetonitrile-based solution containing pyrrole and the electrolyte must be prepared so that the base polymer film is insoluble, but the monomer and electrolyte can diffuse into the film.

Figure 1 shows the relationship between the conductivity of the poly(vinyl chloride) (PVC) film and the polymerization time of the pyrrole. PVC which is a representative commercial polymer was used to coat Nesa glass as a film (1.2 μm thick), and pyrrole was polymerized in the acetonitrile solution containing tetraethylammonium perchlorate. The electrical conductivity of the film stripped from Nesa glass was measured by means of a 4-terminal method. The polymerization for 1 minute increased the conductivity of the PVC film by about 12 orders of magnitude. At this stage, the film was still transparent and showed little increase in thickness. This result suggests that networks of electrically conducting polypyrrole filaments are effectively formed throughout the inside of the PVC film. As the polymerization proceeded, the film thickness increased and a conductivity of 12 Ω^{-1} cm^{-1} was achieved after 6 minutes. The conductivity of the films can be controlled by the polymerization time.

The resultant films are black (some darker than others) and have good surface smoothness. While the original polypyrrole films are hard and relatively fragile, particularly in thin film form, PVC based conducting films are soft, strong, and very easy to handle even at about 1 μm thickness, because of the excellent film qualities of PVC.

We have confirmed that various polymers including poly(vinylidene chloride) copolymers, polystyrenes, polymethacrylates, poly(vinyl ethers), and phenol resins, can be converted into highly conducting films, by adjusting the polymerization conditions. Thus, this process can provide a new type of polymer alloy and a wide variety of novel electrically conducting polymers.

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